DERWENT-ACC-NO: 2002-701189

DERWENT-WEEK: 200444

COPYRIGHT 2004 DERWENT INFORMATION LTD

TITLE: Electrically-conductive **rubber** composition useful as molding material, comprises **ethylene oxide/propylene oxide**/allyl **glycidyl** ether terpolymer **rubber,** **acrylonitrile**/butadiene copolymer **rubber** and quaternary ammonium salt

PATENT-ASSIGNEE: SUMITOMO **RUBBER** IND LTD[SUMR]

PRIORITY-DATA: 2001JP-0009102 (January 17, 2001) , 2001JP-0025898 (February 1, 2001)

Decent primary ref

PATENT-FAMILY:

PUB-NO	PAGES	MAIN-IPC	PUB-DATE	LANGUAGE
JP 3540278 B2	017	C08L 071/02	July 7, 2004	N/A
JP 2002212413 A	012	C08L 071/02	July 31, 2002	N/A
CN 1366002 A	000	C08L 063/00	August 28, 2002	N/A

APPLICATION-DATA:

PUB-NO	APPL-DATE	APPL-DESCRIPTOR	APPL-NO
JP 3540278B2	January 17, 2001	N/A	2001JP-0009102
JP 3540278B2	N/A	Previous Publ.	JP2002212413
JP2002212413A	January 17, 2001	N/A	2001JP-0009102
CN 1366002A	January 16, 2002	N/A	2002CN-0102325

INT-CL (IPC): C08K005/19, C08K005/42 , C08L009/02 , C08L063/00 , C08L071/02 , F16C013/00 , G03G015/02 , G03G015/08 , G03G015/16 , H01B001/00 , H01B001/20

RELATED-ACC-NO: 2002-687116

ABSTRACTED-PUB-NO: JP2002212413A

BASIC-ABSTRACT:

NOVELTY - An electrically-conductive **rubber** composition (I) comprises (parts by weight):

(A) electrically-conductive polymer composition comprising: 70-5 wt.% (A1) **ethylene oxide** (50-95 mol.%)/**propylene oxide** (1-49 mol.%)/allyl **glycidyl** ether (1-10 mol.%) terpolymer with Mn at least 10,000; and 30-95 wt.% (A2) **acrylonitrile**/butadiene copolymer **rubber** (100); and

(B) halogen-free quaternary ammonium salt (0.1-7.0).

USE - (I) is useful as material for the preparation of electrically conductive rollers or belts of e.g. copying machines or printers (claimed).

ADVANTAGE - (I) gives rollers and belts having high dimensional stability, low volume resistivity, small permanent set and good resistance to ozone.

CHOSEN-DRAWING: Dwg.0/2

TITLE-TERMS: ELECTRIC CONDUCTING **RUBBER** COMPOSITION USEFUL MOULD MATERIAL
COMPRISE **ETHYLENE OXIDE PROPYLENE OXIDE** ALLYL **GLYCIDYL** ETHER
TERPOLYMER **RUBBER ACRYLONITRILE** BUTADIENE COPOLYMER **RUBBER**
QUATERNARY AMMONIUM SALT

DERWENT-CLASS: A89 E12 E16 G08 P84 Q62 S06 T04 X12

CPI-CODES: A04-B04; A05-H01B; A07-A04E; A08-M09A; A09-A03; A12-L05C1; A12-W07;
E10-A07; E10-A09B7; E10-A22E; G05-F; G06-G05;

EPI-CODES: S06-A05C; S06-A15; T04-G04; X12-D01X;

CHEMICAL-CODES:
Chemical Indexing M3 *01*
Fragmentation Code
G013 G100 H181 H401 H481 K0 K431 K432 L722 M210
M211 M220 M224 M231 M240 M273 M281 M283 M312 M320
M321 M332 M342 M383 M391 M414 M510 M520 M531 M540

M620 M630 M650 M772 M781 M904 M905 Q130 Q346 R043
Specfic Compounds
A8CJXK A8CJXU

Chemical Indexing M3 *02*
Fragmentation Code
H181 H4 H401 H405 H481 H484 H8 J011 J171 L722
M210 M211 M220 M224 M231 M273 M280 M283 M312 M315
M321 M332 M342 M344 M349 M381 M383 M391 M416 M620
M650 M781 M904 M905 Q130 Q346 R043
Specfic Compounds
A8FRGK A8FRGU

SECONDARY-ACC-NO:
CPI Secondary Accession Numbers: C2002-199239
Non-CPI Secondary Accession Numbers: N2002-552805

MENU SEARCH INDEX DETAIL JAPANESE

1 / 1

* NOTICES *

JPO and NCIPI are not responsible for any
damages caused by the use of this translation.

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention is used for a conductive rubber constituent, conductive vulcanized rubber, and a list in detail about a conductive rubber roller and a conductive rubber belt effective in electrification rollers, such as a copy machine and a printer, a developing roller, a toner feed roller, an imprint roller, an imprint belt, etc.
[0002]
[Description of the Prior Art] In the electrification roller used for a copy machine, a printer, etc., a developing roller, a toner feed roller, an imprint roller, and an imprint belt, it is necessary to give the moderate stable electric resistance value. Conventionally, there are an approach using the electronic conductive rubber which blended conductive bulking agents, such as powder of a metallic oxide and carbon black, into rubber, and an approach using ion conductive rubber, such as polyurethane rubber, acrylonitrile-butadiene rubber (NBR), and epichlorohydrin rubber, as an approach of giving conductivity to this kind of a roller and a belt.
[0003] In the conductive roller or the conductive belt using the electronic conductive rubber which blended the above-mentioned conductive bulking agent, there is a problem which the electric resistance value does not equip with the fixed electric resistance value depending on applied voltage. Since there is a field where the correlation stabilized between the addition of carbon black and the volume resistivity of rubber is not seen, and an electric resistance value changes with slight change of the addition of carbon black rapidly when carbon black is especially used as a conductive bulking agent, control of an electric resistance value becomes very difficult. In addition, it is converted by the constant formula so that the roller electric resistance value after fabricating on the volume resistivity and the roller of a conductive rubber ingredient may be mentioned later, and it changes with the configurations of a roller (or belt).
[0004] Moreover, since it is hard to distribute a conductive bulking agent to homogeneity in rubber, there is also a problem that an electric resistance value has dispersion in the hoop direction and the cross direction of a roller or a belt. Furthermore, even if dispersion with a big electric resistance value is reduced, dispersion in the electric resistance value in the very small range of mum order still exists. It is in the inclination for the direction of the ion conductive rubber instead of electronic conductive rubber to be fond, and to be used especially in recently [of the technique of high-definition-izing, such as digitization and colorization, / remarkable] from this.
[0005] On the other hand, as an electric conduction agent of the above-mentioned ion conductive rubber, there are conductive oligomer and a conductive plasticizer (for all, Mn is 10000 or less) including polyether structures, such as polyethylene oxide. However, in the ion conductive rubber using the above-mentioned electric conduction agent, there is a problem which is easy to pollute a photo conductor.
[0006] Although there is also a method of using acrylonitrile-butadiene rubber (NBR) and polyurethane rubber in addition to the above, only the resistance more than 109.6-ohmcm (the electric resistance value

of a roller is 108.2ohms) is acquired, and the volume resistivity value of a rubber ingredient cannot respond to what comparatively low electric resistance values, such as a thing for colors, are required as also with an imprint belt or an imprint roller. Moreover, there is a problem that ozone resistance ability is not good, either, only by NBR.

[0007] Therefore, it is common to the above-mentioned application, some electrification rollers, a developing roller, and a toner feed roller to blend epichlorohydrin rubber with the ingredient of independent or others, and to use it, and various proposals are made.

[0008] Moreover, by blending the quarternary ammonium salt which contains perchloric acid ion or chloride ion in ion conductive rubber, such as acrylonitrile-butadiene rubber (NBR), polyurethane rubber, and epichlorohydrin rubber, ionization degree is raised and various attempts in which lower electric resistance will be realized are also made.

[0009] For example, in JP,2000-17118,A, lessening location dispersion of electric resistance and lessening compression set by the low degree of hardness with the conductive polymer constituent characterized by containing organic rubber, such as acrylonitrile-butadiene rubber and epichlorohydrin rubber, carbon black, and electric conduction grant agents, such as perchloric acid quarternary ammonium salt, is proposed.

[0010] Furthermore, in JP,9-132677,A, making easy conductive grant of a rubber constituent and control of an electric resistance value is proposed with the rubber constituent which comes to blend the quarternary ammonium salt of perchloric acid etc. with rubber, such as acrylonitrile-butadiene rubber and epichlorohydrin rubber.

[0011]

[Problem(s) to be Solved by the Invention] However, in the conductive polymer constituent of JP,2000-17118,A, although dispersion in electric resistance is lessened and compression set can be reduced, there is a problem that there is a possibility of generating photo conductor contamination. Furthermore, since perchloric acid quarternary ammonium salt is used and chlorine is included in a constituent, when it is going to carry out incineration processing or is going to decompose and recycle by heat or shearing after use, there is a problem that there are poisonous hydrogen chloride gas and a possibility of generating dioxin depending on processing conditions.

[0012] Moreover, in the rubber constituent of JP,9-132677,A, since reduction of compression set is using perchloric acid quarternary ammonium salt for the top which is not enough and contains chlorine in a constituent, there is a problem that there are poisonous hydrogen chloride gas and a possibility of generating dioxin, by incineration processing after use etc. like the above.

[0013] Furthermore, the epichlorohydrin rubber which is an ion conductive polymer contains the chlorine which is one of the halogens during the polymer presentation like chloroprene rubber (CR), chlorinated polyethylene (CPE), chlorosulfonated polyethylene (CSM), and a vinyl chloride (PVC). Therefore, in a conductive polymer, as well as the above when epichlorohydrin rubber is used, there are poisonous hydrogen chloride gas and a possibility that dioxin may occur.

[0014] In recent years, importance is attached very much to an environmental problem, and it is also a social problem with big generating of a toxic gas or dioxin. For this reason, also in the conductive rubber constituent, it is also requested that developing the ingredient which generates neither a toxic gas nor dioxin at the time of incineration etc. is called for immediately, and it makes recycle possible collectively.

[0015] Moreover, in a conductive rubber constituent, in order to reduce volume resistivity, when the quarternary ammonium salt containing halogens (especially chlorine), such as perchloric acid ion or chloride ion, was blended, or when the conductive polymer containing halogens (especially chlorine), such as epichlorohydrin rubber, is blended, the problem of worsening compression set remarkably also has the part of halogens, such as the chlorine, by the reasons of causing side reaction.

[0016] It makes it the technical problem for volume resistivity to be low, and for compression set to be small, and to excel in ozone resistance, to offer the conductive rubber constituent which does not generate photo conductor contamination, either, and conductive vulcanized rubber, to excel in endurance or dimensional stability and to offer an environment-friendly conductive rubber roller and a conductive

rubber belt further, while this invention was made in view of the above-mentioned problem, controls toxic-material generating at the time of incineration etc. and makes recycle possible.
[0017]
[Means for Solving the Problem] In order to solve the above-mentioned technical problem, the copolymerization ratio of this invention of ethyleneoxide / propylene oxide / allyl glycidyl ether is 50-95-mol %/1 - 49-mol %/1 - ten-mol %. The ethyleneoxide-propylene oxide-allyl-glycidyl-ether ternary polymerization object whose number average molecular weight Mn is 10000 or more (A), The above-mentioned conductive polymer 100 weight section is received including the conductive polymer which mixed acrylonitrile-butadiene rubber (B) by the weight ratio of (A):(B) =70:30-5:95. The conductive rubber constituent characterized by coming to blend non-halogen system quarternary ammonium salt at a rate below the 7.0 weight sections more than the 0.1 weight section is offered.
[0018] As mentioned above, since non-halogen system quarternary ammonium salt is used for the conductive rubber constituent of this invention at a specific rate, a conductive polymer and a halogen component cannot cause side reaction, and it can reduce compression set. Furthermore, it can be compatible and reduction of volume resistivity and improvement in ozone resistance can also be realized. Moreover, as mentioned above, the mutual copolymerization ratio of an ethyleneoxide-propylene oxide-allyl-glycidyl-ether ternary polymerization object is specified, and this ternary polymerization object and acrylonitrile-butadiene rubber (NBR) are mixed at a specific rate. Thereby, reduction of compression set is realizable in the range which does not spoil ozone resistance ability. Furthermore, since the conductive polymer containing halogens, such as epichlorohydrin rubber, is not used, it is the constituent of a non-halogen system as a whole, and when processing incineration etc. after use, there is no possibility of generating harmful matter, such as hydrogen chloride gas.
[0019] Thereby, in conventional ion conductive rubber, the good physical properties (the dimensional stability which volume resistivity is low, is small, is excellent in ozone resistance, and does not have photo conductor stain resistance is good) as the conductive rubber roller which was not able to be realized, and a conductive rubber belt can be acquired, and it is kind also to an environment, and the rubber goods suitable for practical use can be offered. [of compression set]
[0020] Acrylonitrile-butadiene rubber (B) is mixed with the above-mentioned ethyleneoxide-propylene oxide-allyl-glycidyl-ether ternary polymerization object (A) by the weight ratio of (A):(B) =70:30-5:95. If there is a problem that photo conductor contamination occurs and the weight of acrylonitrile-butadiene rubber (B) becomes large from the above-mentioned weight ratio, while compression set will become large, if the weight of acrylonitrile-butadiene rubber (B) becomes smaller than the above-mentioned weight ratio, while causing ozone degradation, since own volume resistivity of NBR is high, because there is a problem that volume resistivity will go up conversely, it is considering as the above-mentioned convention range. moreover, the thing to mix in the above-mentioned weight ratio -- the former -- acrylonitrile-butadiene rubber -- if independent, while the low electric resistance which was not able to be realized is acquired and also being able to improve ozone resistance, when it considers as a conductive rubber roller or a conductive rubber belt, gloss is shown in a front face and the extrusion condition that there is no wrinkling can obtain a very good thing.
[0021] It is based on the following reasons that the copolymerization ratio of the above-mentioned ethyleneoxide (it is also called Following EO) / propylene oxide (it is also called Following PO) / allyl glycidyl ether (it is also called Following AGE) is made into 50-95-mol %/1 - 49-mol %/1 - ten-mol %.
[0022] Among a conductive rubber constituent, the oxonium-ion metallurgy group cations in a polymer (for example, nickel ion contained in a polymer antioxidant) or ammonium ion (based on quarternary ammonium salt) is stabilized in an ethyleneoxide unit etc., and depends on it being carried by the segmental motion of the chain of the part that conductivity is demonstrated. Therefore, the one where the ratio of an ethyleneoxide unit is higher can stabilize many ion, and is considered that it can demonstrate low resistance-ization. However, if the ratio of ethyleneoxide is gathered too much, since crystallization of ethyleneoxide will take place and the segmental motion of a chain will be barred, volume resistivity goes up conversely. Propylene oxide is copolymerized in order to control crystallization by this ethyleneoxide.

[0023] As for the conductive rubber constituent of this invention, it is desirable to make the volume resistivity value into the range of 107.0-ohmcm - 109.0-ohmcm. This is difficult to realize a conductive rubber constituent with a volume resistivity value smaller than 107.0-ohmcm by ion conductive rubber, and is because it depends on carbon electric conduction isoelectronic conductive resin and does not spread on it. Moreover, when the volume resistivity value was larger than 109.0-ohmcm and it considers as a rubber roller or a rubber belt, it is because there is a problem of effectiveness, such as an imprint, and electrification, toner supply, falling and stopping being suitable for practical use. in addition, the Measuring condition of a volume resistivity value -- the constant temperature of 55% of 23-degree-C relative humidity -- it is referred to as applied-voltage 500V under the constant humidity condition.

[0024] Maintaining the physical properties (the dimensional stability which compression set is small, is excellent in ozone resistance, and photo conductor contamination does not generate is good) of the above-mentioned conductive rubber constituent, the mutual copolymerization ratio of the above-mentioned ethyleneoxide, propylene oxide, and the ternary polymerization object of allyl glycidyl ether was set up, and the weight rate of this 3 yuan polymer and acrylonitrile-butadiene rubber and the weight rate of non-halogen system quarternary ammonium salt are specified so that it may become the above-mentioned volume resistivity value. The effectiveness that it will become inadequate stabilizing [of ion] ethyleneoxide less than [50 mol %] if propylene oxide exceeds 49-mol %, and it reduces a volume resistivity value becomes small. On the other hand, while ethyleneoxide exceeds 95-mol %, there is a problem on which volume resistivity goes up that propylene oxide is less than [1 mol %] too much. Moreover, when a degree of hardness rises too much by crystallization also in physical properties and it uses as a roller or a belt, there is a problem which stops being suitable for practical use.

[0025] While bridge formation is made possible, and it is [bleeding or photo conductor contamination] lifting-hard and carrying out them by this by copolymerizing the above-mentioned allyl glycidyl ether, rubber elasticity is given and physical properties are raised. Moreover, from this allyl-glycidyl-ether unit itself obtaining free volume as a side chain, the above-mentioned crystallization can be controlled further and it is based on having found out that low resistance-ization which therefore is not in the former was realizable. If making the copolymerization ratio of allyl glycidyl ether into 1-10-mol % exceeds ten-mol % while generating of bleeding or photo conductor contamination becomes easy to take place less than [1 mol %], the depressor effect of crystallization beyond it will not be acquired, but the number of the points after vulcanization constructing a bridge will increase, and low resistance-ization will not be able to be realized on the contrary, and tensile strength, a fatigue property, flexibility, etc. will get worse.

[0026] Thus, while suppressing crystallization of ethyleneoxide and lowering volume resistivity by copolymerizing allyl glycidyl ether, the double bond between carbon-carbon is introduced by copolymerization of allyl glycidyl ether, and bridge formation with other rubber is enabled. Bleeding and photo conductor contamination can be prevented by carrying out a joint use pons to other rubber. Furthermore, due to a joint use pons with other rubber, since molecular weight is also large and it can carry out, even if the above-mentioned ethyleneoxide-propylene oxide-allyl-glycidyl-ether ternary polymerization object blends a remarkable daily dose, bleeding and photo conductor contamination stop being able to happen easily.

[0027] The number average molecular weight Mn of the above-mentioned ethyleneoxide-propylene oxide-allyl-glycidyl-ether ternary polymerization object (it is also called below an EO-PO-AGE ternary polymerization object) is carrying out for preventing bleeding and photo conductor contamination to 10000 or more.

[0028] Non-halogen system quarternary ammonium salt is blended at a rate below the 7.0 weight sections more than the 0.1 weight section to the above-mentioned conductive polymer 100 weight section. If there is less non-halogen system quarternary ammonium salt than the 0.1 weight section, because reduction of volume resistivity cannot be aimed at efficiently, it will consider as the above-mentioned range. Moreover, when there is more non-halogen system quarternary ammonium salt than the 7.0 weight sections, it is for photo conductor contamination to arise.

[0029] Moreover, by having the problem of photo conductor contamination, when the above-mentioned

EO-PO-AGE ternary polymerization object is blended in large quantities, and blending non-halogen system quarternary ammonium salt, although implementation of low electric resistance will become difficult if the amount of blends is restricted to the range in which photo conductor contamination does not take place, even if it reduces the amount of the EO-PO-AGE ternary polymerization object used, it becomes possible to realize low electric resistance efficiently. Thereby, the problem of photo conductor contamination can also be controlled, maintaining low electric resistance. Moreover, by blending non-halogen system quarternary ammonium salt, since the amount of the expensive EO-PO-AGE ternary polymerization object used is reduced and low electric resistance can be realized, it is advantageous also in cost.

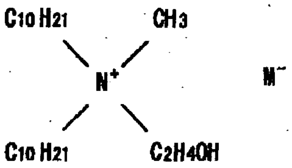
[0030] The quarternary ammonium salt of a sulfonic acid or the quarternary ammonium salt of a gluconic acid can be especially used for the above-mentioned non-halogen system quarternary ammonium salt suitably. As a result of studying the reason for the above wholeheartedly about the skeletal structure of non-halogen system quarternary ammonium salt, since especially ionization degree is high, the two above-mentioned sorts of ammonium salt is based on the ability also of photo conductor contamination for low electric resistance to be realized efficiently, and for compression set to be turned small up, and to be controlled.

[0031] As non-halogen system quarternary ammonium salt, quarternary ammonium salt, such as a sulfuric acid and a nitric acid, can be used besides the two above-mentioned sorts. Thus, it is the salt of a comparatively strong acid and a thing with the structure which does not contain halogens, such as chlorine, is good.

[0032] Specifically as non-halogen system quarternary ammonium salt, the thing of the structure shown by the following formulas 1 (** 1) is mentioned.

[0033]

[Formula 1]



[0034] As an example of the quarternary ammonium salt of a sulfonic acid, that whose M is p-toluenesulfonic-acid residue is mentioned among the above-mentioned formula. (Trade name: KP-4728, Kao Corp. make) As an example of the quarternary ammonium salt of a gluconic acid, that whose M is glucono lactone acid residue is mentioned among the above-mentioned formula. (Trade name: KP-4729, Kao Corp. make)

[0035] As for the above-mentioned acrylonitrile-butadiene rubber (B), it is desirable to contain liquefied acrylonitrile-butadiene rubber (NBR). Thus, since it will be easy to move a polymer chain, and it excels also in workability and the transportation efficiency of ion also becomes high, volume resistivity also becomes [if the acrylonitrile-butadiene rubber (NBR) containing liquefied NBR is used,] low. Moreover, since extrusion nature is good, the conductive roller and the conductive belt which there is no wrinkling and had a good surface state can be obtained.

[0036] Also in the acrylonitrile-butadiene rubber containing liquefied acrylonitrile-butadiene rubber, the thing especially with a high acrylonitrile content has good compatibility with the above-mentioned EO-PO-AGE ternary polymerization object (A), its effectiveness which makes good the rubber skin at the time of extrusion after kneading is very high, and since the effectiveness of lowering the degree of hardness of vulcanizate is also large, it is very suitable.

[0037] Furthermore, since the mixture of the amount NBR of macromolecules and liquefied NBR can prevent photo conductor contamination and can keep the physical properties of a rubber constituent good as acrylonitrile-butadiene rubber (NBR), it is used especially suitably. Specifically, the Nippon Zeon Co., Ltd. make and NIPPORU DN223 (trade name) are mentioned.

[0038] As the above-mentioned acrylonitrile-butadiene rubber (NBR), diene system rubber with high above-mentioned ethyleneoxide-propylene oxide-allyl-glycidyl-ether ternary polymerization object and compatibility is suitable. as the example of such rubber -- inside nitril and the crown -- the various kinds NBR of nitril, high nitril, and pole quantity nitril are mentioned. Thereby, a very good constituent can be obtained also in respect of physical properties, such as compression set and a degree of hardness.

[0039] It sets to the conductive vulcanized rubber which vulcanized the above-mentioned conductive rubber constituent, and is JIS. By the permanent-set examining method of the vulcanized rubber of a publication, the measurement temperature of 70 degrees C and the magnitude of the compression set measured in measuring-time 24 hours may be 25% or less K6262. When this has the value of the above-mentioned compression set larger than 25%, it is because the dimensional change when becoming a roller becomes large too much and it is not suitable for practical use. Although the difference of how many minutes is produced according to expansion ratio or a foaming gestalt when using as foam especially (it is made sponge), it is desirable that it is the above-mentioned range.

[0040] As a vulcanization system, since it is compatible in low electric resistance and low stain resistance, the sulfur vulcanization system is suitable. As a class of accelerator, it is desirable to have combined dibenzothiazyl disulfide and tetramethylthiurammonosulfide. In addition, 2-mercaptobenzothiazole etc. may be used instead of dibenzothiazyl disulfide. If the vulcanization system of (Sulfur S) / (dibenzothiazyl disulfide DM) / tetramethylthiurammonosulfide (TS), or (Sulfur S) / (2-mercaptobenzothiazole M) / tetramethylthiurammonosulfide (TS) is used especially, while being able to carry out a joint use pons efficiently and being able to reduce photo conductor contamination, it is desirable in order to reduce compression set.

[0041] Furthermore, as a vulcanization system by a suitable vulcanizing agent and a suitable vulcanization accelerator, the vulcanization system blended at a rate of sulfur / dibenzothiazyl disulfide / tetramethylthiurammonosulfide =1.5/1.5/0.5, or sulfur / 2-mercaptobenzothiazole / tetramethylthiurammonosulfide =1.5/1.5/0.5 is mentioned. Vulcanizing time turns short up by this, the joint use pons of the three components each of the above-mentioned EO-PO-AGE ternary polymerization object, acrylonitrile-butadiene rubber, and non-halogen system quarternary ammonium salt can be carried out well, and the possibility of photo conductor contamination can be reduced.

[0042] Vulcanization can be performed by the usual approach, for example, it may vulcanize in the vulcanizer under steam pressurization, or you may vulcanize with press cure, and secondary vulcanization may be performed if needed. Moreover, vulcanizing by the peroxide vulcanization system is also possible, and photo conductor contamination can be controlled by combining with secondary vulcanization.

[0043] The conductive rubber constituent of this invention blends the above-mentioned EO-PO-AGE ternary polymerization object, acrylonitrile-butadiene rubber, and non-halogen system quarternary ammonium salt in the above-mentioned convention range, further, is a constituent of the non-halogen system containing the various compounding agents (a vulcanization accelerator, a bulking agent, carrier acid, antioxidant, etc.) blended a vulcanizing agent and if needed, and is manufacturing conductive vulcanized rubber by carrying out melting kneading and vulcanizing these. Melting kneading can be performed by the usual approach. For example, it is kneading about 2 to 10 minutes at 40 degrees C - 130 degrees C using well-known rubber kneading equipments, such as an opening roll and a direct-vent-system kneading machine.

[0044] From the conductive vulcanized rubber obtained by vulcanizing the above-mentioned conductive rubber constituent, the conductive rubber roller and the conductive rubber belt are fabricated. The conductive vulcanized rubber of this invention has low volume resistivity, and is excellent in the point that compression set is small, upwards, is excellent also in ozone resistance, and does not generate photo conductor contamination, either. Moreover, since it is a non-halogen system, a toxic gas does not occur at the time of incineration. Therefore, in the conductive rubber roller using this, an electric resistance value is low, and since it excels also in the above and other physical properties, when low electric resistance values, such as the imprint roller and electrification roller for colors, a toner feed roller, and a developing roller, are required, it is used especially suitably. Furthermore, since a toxic gas is not generated at the time of incineration etc., decomposition by heat or shearing also becomes easy and an environment-friendly product can be offered.

[0045] After being able to create the above-mentioned conductive rubber roller with a conventional method, for example, preforming the above-mentioned conductive rubber constituent (kneading object) in the shape of a tube with a single screw extruder, and vulcanizing 160 degrees C of this preforming article for 10 to 60 minutes, and it inserts rodding and grinds a front face, it can be cut into a necessary dimension and conventionally well-known various approaches, such as considering as a roller, can be used for it. Vulcanizing time is good to decide in quest of optimum cure time amount with the rheometer for a vulcanization trial (example: curelast meter). Moreover, vulcanizing temperature may be gone up and down and set to the above-mentioned temperature if needed.

[0046] Moreover, after the above-mentioned conductive rubber belt extrudes the above-mentioned conductive rubber constituent (kneading object) in the shape of a belt with an extruding press machine and fabricates it, it can perform 160 degrees C and 10 - 60-minute vulcanization, and the conventionally well-known various approaches of creating the body of a belt can be used for it. Vulcanizing temperature may be gone up and down and set to the above-mentioned temperature if needed.

[0047]

[Embodiment of the Invention] Hereafter, the operation gestalt of this invention is explained. The conductive rubber constituent of the first operation gestalt of this invention The copolymerization ratio of ethyleneoxide / propylene oxide / allyl glycidyl ether The ethyleneoxide-propylene oxide-allyl-glycidyl-ether ternary polymerization object (A) whose number average molecular weight Mn it is 90 mol %/4 mol %/6 mol %, and is 80000 25 weight sections, Non-halogen system quarternary ammonium salt is blended at a rate of 5 weight sections to the above-mentioned conductive polymer 100 weight section including the conductive polymer which mixed acrylonitrile-butadiene rubber (B) by the weight ratio of 75 weight sections, (A):(B) =25:75 [i.e.,].

[0048] furthermore, the above-mentioned conductive polymer 100 weight section -- receiving -- a vulcanizing agent (sulfur) -- 5 weight sections came out of 20 weight sections and a zinc oxide, 1 weight section came out of stearin acid comparatively, the 1.5 weight section and a vulcanization accelerator 2 (tetramethylthiurammonosulfide) are blended for the 0.5 weight section and an inorganic bulking agent, and the chlorine content makes 0wt% the 1.5 weight section and a vulcanization accelerator 1 (dibenzothiazyl disulfide).

[0049] The above-mentioned non-halogen system quarternary ammonium salt is made into the quarternary ammonium salt of a gluconic acid. Moreover, the thing which made the usual acrylonitrile-butadiene rubber 100 weight section contain liquefied acrylonitrile-butadiene rubber at a rate of 50 weight sections is used for the above-mentioned acrylonitrile-butadiene rubber in the above-mentioned weight section.

[0050] Using well-known rubber kneading equipments, such as a direct-vent-system kneading machine, melting kneading was carried out and the above-mentioned conductive rubber constituent which blended various compounding agents a conductive polymer, non-halogen system quarternary ammonium salt, a vulcanizing agent, and if needed is vulcanized. This has obtained the conductive vulcanized rubber used for a conductive rubber roller etc.

[0051] The above-mentioned conductive vulcanized rubber is JIS. In the permanent-set examining method of vulcanized rubber given in K6262, the measurement temperature of 70 degrees C and the compression set measured in measuring-time 24 hours are 22%.

[0052] moreover, the above-mentioned conductive vulcanized rubber -- the constant temperature of 55% of 23-degree-C relative humidity -- in the Measuring condition of applied-voltage 500V, a volume resistivity value is 108.2 under a constant humidity condition.

[0053] Moreover, after preforming the above-mentioned conductive polymer constituent in the shape of a tube with a single screw extruder, vulcanizing 160 degrees C of this preforming article for 10 to 60 minutes, inserting rodding and grinding a front face, it cuts into a necessary dimension and is considering as the roller for an imprint. As shown in drawing 1 , the conductive rubber roller 1 for the above-mentioned imprint is a cylindrical shape-like, and an axis 2 is inserted in the inner circumference, and it is in it.

[0054] Thereby, a volume resistivity value is low, since compression set is also small, it excels in dimensional stability and endurance, and excels in ozone resistance, and the conductive rubber roller which also had photo conductor contamination controlled can be obtained. Furthermore, since it is a non-halogen system, a conductive rubber roller good for the environment which a pollutant does not generate in the incineration after use etc. can be obtained.

[0055] In addition, in this operation gestalt, although the conductive rubber roller was created from the above-mentioned conductive rubber constituent as a roller for an imprint, it cannot be overemphasized that this conductive rubber constituent is used as conductive rubber rollers, such as an electrification roller, a developing roller, and a toner feed roller. Moreover, various foaming agents may be blended with a conductive rubber constituent, and you may use as a foaming roll etc.

[0056] In addition, it cannot be overemphasized as non-halogen system quarternary ammonium salt that the quarternary ammonium salt of a sulfonic acid etc. may be used.

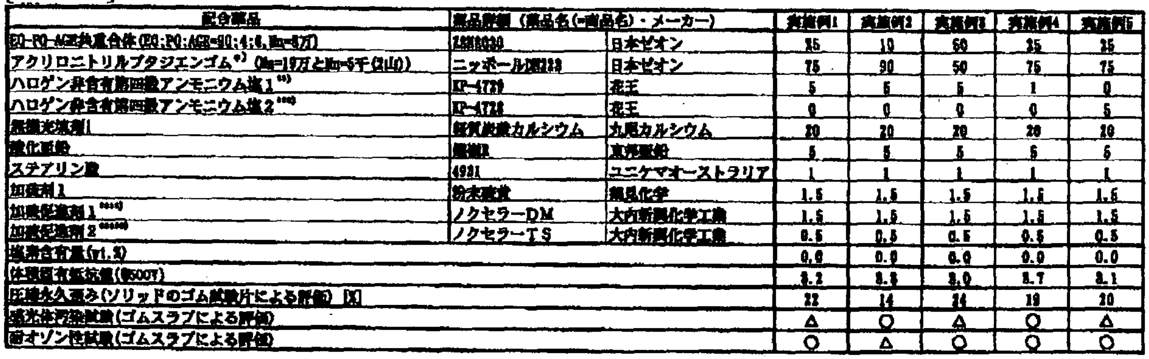
[0057] Moreover, as shown in drawing 2 , the conductive rubber belts 3, such as an imprint belt, are created from the conductive rubber constituent. The conductive rubber belt 3 imprints the toner image which was made the firm-bridging condition by two or more pulleys 4, and supported and conveyed the web materials 6, such as paper, by them into the straight-line-like part 5 of the conductive rubber belt 3 top which rotates, and was made on the photo conductor to a web material 6.

[0058] Hereafter, the examples 1-5 and the examples 1-7 of a comparison of a conductive rubber constituent of this invention are explained in full detail.

[0059] About examples 1-5 and the examples 1-7 of a comparison, the ingredient (combination chemical) which becomes the following Table 1 and 2 from combination of a publication respectively was kneaded with each loadings with the direct-vent-system kneading machine (DS10-40 MWA-S, Made in the Moriyama Factory). The rubber which picked the ribbon from the above-mentioned kneading machine was extruded with the roller head extruder, it fabricated in the shape of a sheet, it was taught to metal mold, optimal time amount press cure was carried out at 160 degrees C, and the vulcanization rubber slab sheet for physical-properties evaluation was created.

[0060]

[Table 1]



配合薬品	薬品詳細（薬品名(=商品名)・メーカー）		実施例1	実施例2	実施例3	実施例4	実施例5
EO-PO-AGE共重合体(EO:PO:AGE=90:4:6, Mw=47万)	ZSN8030	日本ゼオン	25	10	50	25	25
アクリロニトリルブタジエンゴム*) (Mw=19万とMw=5千(2山))	ニッポールDN223	日本ゼオン	75	90	50	75	75
ハロゲン非含有第四級アンモニウム塩1**)	KP-4729	花王	5	5	5	1	0
ハロゲン非含有第四級アンモニウム塩2***)	KP-4728	花王	0	0	0	0	5
無機充填剤1	軽質炭酸カルシウム	丸尾カルシウム	20	20	20	20	20
酸化亜鉛	銀嶺R	東邦亜鉛	5	5	5	5	5
ステアリン酸	4931	ユニケマオーストラリア	1	1	1	1	1
加硫剤1	粉末硫黄	鶴見化学	1.5	1.5	1.5	1.5	1.5
加硫促進剤1****)	ノクセラーDM	大内新興化学工業	1.5	1.5	1.5	1.5	1.5
加硫促進剤2*****)	ノクセラーTS	大内新興化学工業	0.5	0.5	0.5	0.5	0.5
塩素含有量(wt.%)			0.0	0.0	0.0	0.0	0.0
体積固有抵抗値(@500V)			8.2	8.3	8.0	8.7	8.1
圧縮永久歪み(ソリッドのゴム試験片による評価) [%]			22	14	24	19	20
感光体汚染試験(ゴムスラブによる評価)			△	○	△	○	△
耐オゾン性試験(ゴムスラブによる評価)			○	△	○	○	○

[0061]

[Table 2]

配合薬品	薬品詳細（薬品名(=商品名)・メーカー）		比較例1	比較例2	比較例3	比較例4	比較例5	比較例6	比較例7
EO-PO-AGE共重合体(EO:PO:AGE=90:4:6, Mn=8万)	ZSN8030	日本ゼオン	25	0	75	25	25	25	0
アクリロニトリルブタジエンゴム(Mn=19万とMn=5千(2:1))	ニッポールDN223	日本ゼオン	75	100	25	75	75	75	50
エピクロルヒドリンゴム(EO:EP:AGE=56:40:4, Mn=14万)	エピクロマーCG102	ダイソー	0	0	0	0	0	0	50
ハロゲン非含有第四級アンモニウム塩1	KP-4729	花王	0	5	5	10	0	0	0
ハロゲン非含有第四級アンモニウム塩2	KP-4728	花王	0	0	0	0	10	0	0
ハロゲン含有第四級アンモニウム塩1 [illegible]	コータミン86Pコンク	花王	0	0	0	0	0	5	0
合成ハイドロタルサイト	DHT-4A-2	協和化学	0	0	0	0	0	0	1.5
無機充填剤1	軽質炭酸カルシウム	丸尾カルシウム	20	20	20	20	20	20	20
酸化亜鉛	銀嶺R	東邦亜鉛	5	5	5	5	5	5	5
ステアリン酸	4931	ユニケマオーストラリア	1	1	1	1	1	1	1
加硫剤1	粉末硫黄	鶴見化学	1.5	1.5	1.5	1.5	1.5	1.5	1.5
加硫促進剤1	ノクセラーDM	大内新興化学工業	1.5	1.5	1.5	1.5	1.5	1.5	1.5
加硫促進剤2	ノクセラーTS	大内新興化学工業	0.5	0.5	0.5	0.5	0.5	0.5	0.5
塩素含有量(wt.%)			0.0	0.0	0.0	0.0	0.0	0.3	8.4
体積固有抵抗値(@500V)			9.1	9.0	7.7	7.8	7.7	7.8	8.8
圧縮永久歪み(ソリッドのゴム試験片による評価) [%]			19	9.3	25	25	23	20	20
感光体汚染試験(ゴムスラブによる評価)			○	○	×	×	×	○	○
耐オゾン性試験(ゴムスラブによる評価)			△	×	○	○	○	○	○

[0062] The numeric value of the upper case in each above-mentioned table (up to a vulcanization accelerator) is the weight section. The unit of a chlorine content is weight % and the unit of compression set is %. Moreover, in ethyleneoxide and PO, propylene oxide and AGE express allyl glycidyl ether, and EP expresses [Abbreviation EO] epichlorohydrin.

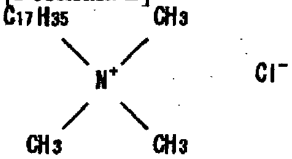
[0063] Moreover, with acrylonitrile-butadiene rubber, the thing which made the usual acrylonitrile-butadiene rubber 100 weight section contain liquefied acrylonitrile-butadiene rubber at a rate of 50 weight sections was used in the weight section in each table among each above-mentioned table.

[0064] As halogen non-containing quarternary ammonium salt 1 (non-halogen system quarternary ammonium salt), KP-4729 (glucono lactone acid chloride) mentioned above was used. As halogen non-containing quarternary ammonium salt 2 (non-halogen system quarternary ammonium salt), KP-4728 (p-toluenesulfonic-acid salt) mentioned above was used respectively.

[0065] In the example of a comparison, the thing (Kohtamin 86P concentrated ** Kao Corp. make) of the structure shown by the formula 2 (** 2) of the following containing chlorine as halogen content quarternary ammonium salt 1 was used.

[0066]

[Formula 2]



[0067] The vulcanization accelerator 1 was made into dibenzothiazyl disulfide, and the vulcanization accelerator 2 was made into tetramethylthiurammonosulfide.

[0068] (An example 1 thru/or example 5) The test piece which is mixed to what was used with the compounding ratio of the above-mentioned convention which shows an EO-PO-AGE ternary polymerization object and acrylonitrile-butadiene rubber in Table 1 with the compounding ratio which shows the non-halogen system quarternary ammonium salt mentioned above in Table 1, and becomes it from a conductive rubber constituent by the above-mentioned approach was obtained.

[0069] (The example 1 of a comparison thru/or example 7 of a comparison) Although used for this invention which shows an EO-PO-AGE ternary polymerization object and acrylonitrile-butadiene rubber in Table 2 with the regular compounding ratio in the example 1 of a comparison, non-halogen system quarternary ammonium salt was not blended. In the example 2 of a comparison, it blended only with acrylonitrile-butadiene rubber with the compounding ratio which shows non-halogen system quarternary ammonium salt 1 in Table 2. In the example 3 of a comparison, it blended with what was used out of the convention range of the compounding ratio of this invention which shows an EO-PO-AGE ternary polymerization object and acrylonitrile-butadiene rubber in Table 2 with the compounding ratio which shows non-halogen system quarternary ammonium salt 1 in Table 2. Although used for this invention which shows an EO-PO-AGE ternary polymerization object and acrylonitrile-butadiene rubber in Table 2 with the regular compounding ratio in the example 4 of a comparison, and the example 5 of a comparison, non-halogen system quarternary ammonium salt 1 (example 4 of a comparison) and non-halogen system quarternary ammonium salt 2 (example 5 of a comparison) were respectively blended with the compounding ratio outside the convention range of this invention shown in Table 2. Although used for this invention which shows an EO-PO-AGE ternary polymerization object and acrylonitrile-butadiene rubber in Table 2 with the regular compounding ratio in the example 6 of a comparison, it blended with the compounding ratio which shows halogen content quarternary ammonium salt 1 in Table 2. In the example 7 of a comparison, non-halogen system quarternary ammonium salt was not blended using acrylonitrile-butadiene rubber and epichlorohydrin rubber.

[0070] The following property measurement was performed about the test piece which consists of a conductive rubber constituent of each example created as mentioned above and each example of a comparison. The result is shown in the lower berth of above-mentioned Table 1 and 2.

[0071] (Measurement of a volume resistivity value) above -- a vulcanization rubber slab sheet (130mmx130mmx2mm) -- creating -- digital ultra-high-resistance microammeter R-8340A by ADVANTEST Corporation -- using -- the constant temperature of 55% of 23-degree-C relative humidity -- as the bottom of a constant humidity condition, and applied-voltage 500V -- JIS Volume-resistivity (volume resistivity value) rhoV (omegacm) of a publication was measured to K6911. In addition, the volume resistivity value is shown in Table 1 and Table 2 with the common-logarithm value.

[0072] In addition, in the case of a solid roller with a uniform monolayer, the roller electric resistance R (omega) can be expressed like a degree type.

R (omega) = (rhoV/2pinu) log10 (r1/r2)

rhoV is volume resistivity (ohm-cm) among the above-mentioned formula, nu is roll rubber width of face (cm), r1 is a roll outer diameter (mm), and r2 is a shaft outer diameter (mm). For example, if these

values are assigned when the dimensions of a roller are r1=15, r2=6, and nu= 21.8, it will become like a degree type theoretically.
log10 R (omega) = -2.5 + log10 It rhoV Depends, and if volume resistivity values (omegacm) are 107.0-109.0 (omegacm), with the solid imprint roller of the above-mentioned dimension, the roller electric resistance value R (omega) will be set to 104.5-106.5 (omega). However, in an actual measurement, the numeric value 2.5 in an upper type is set to 1.3-2.0, and the roller electric resistance value R (omega) is set to 105.0-107.7 (omega).
[0073] (Measurement of compression set) JIS It measured in measurement temperature [of 70 degrees C], and measuring-time 24 hours according to the convention of K6262 "the permanent-set test method of vulcanized rubber."
[0074] (Photo conductor contamination trial) Laser made from Hewlett Packard Where each vulcanization rubber slab sheet of an example and the example of a comparison is pushed against the photo conductor set to the cartridge (cartridge type C4127X) of a Jet4000 mold laser beam printer, it is kept for one week under 32.5 degrees C and conditions of 90% of relative humidity. Then, each vulcanization rubber slab sheet was removed from the photo conductor, the above-mentioned printer performed halftone printing using the photo conductor concerned, the dirt existence of printed matter was checked visually, and three steps of the following criteria estimated.
O : with [as long as printed matter is seen by the eye] no contamination.
**: Slight contamination (it is satisfactory on the use which can be taken even to extent which the imprinting of less than five sheets does not see and show by the eye contamination)
x: Serious contamination (contamination which looks at printed matter by the eye, and abnormalities understand although five or more sheets are stenciled)
[0075] (Ozone resistance evaluation) JIS According to the convention of the "ozone deterioration test approach of vulcanized rubber" given in K6259, it examined under 40-degree C temperature conditions, and the degradation situation was evaluated. However, in consideration of the practical use to a conductive roller, 2 ppm and observation time amount made elongation percentage, and the ozone level made them the 50,100,200-hour back 5%. It examined with the rubber slab sheet and the following criteria estimated.
O With no crack also after [of :] 200 hours.
**: It is 50 - 200 hours and is crack initiation.
x: Cut in 50 - 200 hours.
[0076] As shown in Table 1, the copolymerization ratio of ethyleneoxide / propylene oxide / allyl glycidyl ether of an example 1 - an example 5 is 90 mol %/4 mol %/6 mol %. Acrylonitrile-butadiene rubber (B) is received in the ethyleneoxide-propylene oxide-allyl-glycidyl-ether ternary polymerization object (EO-PO-AGE copolymer) (A) whose number average molecular weight Mn is 80,000. (A) It is the conductive rubber constituent of this invention which mixed non-halogen system quarternary ammonium salt below in the 7.0 weight sections more than the 0.1 weight section to the conductive polymer 100 weight section mixed by the weight ratio of :(B) =70:30-5:95.
[0077] The volume resistivity value of the test piece which consists of a conductive rubber constituent of these examples 1 - an example 5 was 108.0-ohmcm - 108.8-ohmcm, and compression set was 14% - 24%. The examples 1, 3, and 5 of evaluation of a photo conductor contamination trial were **s, and examples 2 and 4 were O. Although only the example 2 of evaluation of an ozone resistance trial was **, all other examples were O.
[0078] Thus, the example 1 - the example 5 had the low volume resistivity value, and compression set was small, and there is almost no photo conductor contamination and it has checked on use having the outstanding property that ozone resistance is also good satisfactory. Moreover, it has also checked that they did not have a hydrogen chloride at the time of the processing after use, and the problem of dioxin generating since chlorine content is 0.0% altogether and examples 1-5 do not contain chlorine.
[0079] Furthermore, by blending non-halogen system quarternary ammonium salt, examples 1-5 reduced the amount of the expensive EO-PO-AGE ternary polymerization object used, had realized low electric resistance, and were advantageous also in cost.

[0080] Although the example 1 of a comparison was a constituent with which only the point which does not blend non-halogen system quarternary ammonium salt differs from combination of an example 1, since non-halogen system quarternary ammonium salt was not blended, compared with 108.2-ohmcm of an example 1, the example 1 of a comparison had the volume resistivity value as high as 109.1-ohmcm as shown in Table 2 on the other hand.

[0081] Although the example 2 of a comparison was the constituent which used only acrylonitrile-butadiene rubber as a polymer and blended the halogen quarternary ammonium salt 1 non-containing (non-halogen system), its ozone resistance was unsuitable.

[0082] Although only the point which blended the EO-PO-AGE ternary polymerization object with this invention at more rate rather than the regular compounding ratio was a different constituent from combination of an example 1, the example 3 of a comparison had severe photo conductor contamination, and carried out spec. out. Moreover, the compression set was also 25% and was not so desirable.

[0083] Although only the blended point was a different constituent from combination of an example 1, the example 4 of a comparison had severe photo conductor contamination, and carried out spec. out. Moreover, the compression set was also 25% and was not so desirable.

[0084] Although only the blended point was a different constituent from combination of an example 5, the example 5 of a comparison had severe photo conductor contamination, and carried out spec. out.

[0085] Although only the point which replaced with non-halogen system quarternary ammonium salt, and blended halogen content quarternary ammonium salt was a different constituent from combination of an example 1, since the example 6 of a comparison had blended halogen content quarternary ammonium salt, compression set carries out [it is large and] spec. out to 30% and was unsuitable [the example]. Moreover, since halogen content quarternary ammonium salt is blended and chlorine is contained, the problem which a hydrogen chloride and dioxin generate at the time of the processing after use will arise.

[0086] Although it is the constituent which the example 7 of a comparison blends acrylonitrile-butadiene rubber and epichlorohydrin rubber, and does not blend quarternary ammonium salt, since the epichlorohydrin rubber containing chlorine is blended, the problem which a hydrogen chloride and dioxin generate at the time of the processing after use will arise.

[0087]

[Effect of the Invention] Since the ethyleneoxide-propylene oxide-allyl-glycidyl-ether ternary polymerization object with which number average molecular weight Mn is 10000 or more, and consists of a specific copolymerization ratio is blended to acrylonitrile-butadiene rubber in the specific blending ratio of coal according to this invention so that more clearly than the above explanation, photo conductor contamination is also controlled low [a volume resistivity value] in the top where compression set is small, and the good conductive rubber constituent of ozone resistance can be obtained.

[0088] Moreover, according to this invention, since non-halogen system quarternary ammonium salt is used, low volume resistivity can be obtained upwards and compression set can be reduced. Furthermore, by considering as a non-halogen system as the whole constituent, when processing incineration etc. after use, there is no possibility that the harmful matter of the halogen origins, such as hydrogen chloride gas, may be generated, and it can consider as a conductive rubber constituent good for an environment.

[0089] Thus, a volume resistivity value is low, and since it excels in practicality, such as endurance and dimensional stability, the rubber roller and rubber belt using a conductive rubber constituent of this invention can be suitably used in an imprint belt or an imprint roller. Since a toxic gas is not generated even if the object for colors, the thing for high definition, etc. try decomposition by heat or shearing after use especially by the ability using it suitably as a conductive rubber roller and a conductive rubber belt also in a process of which low resistance is required, the above decomposition is easy and an environment-friendly product can be offered.

[Translation done.]